ABSORPTION OF MICROWAVES IN CYCLOHEXANOL AND CYCLOPENTANOL AND THEIR SOLUTIONS

T J BHATTACHARYYA

Optics Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32.

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ABSTRACT. The absorption of 3.18 cm microwaves in cyclohexanol, cyclopentanol, and their solutions in heptane and carbon tetrachloride was studied at different temperatures. The solution in CCl_4 did not show any absorption. The temperature-attenuation curves show maxima at 105°C, 96°C, 14°C and 8°C respectively in the cases of cyclohexanol, cyclopentanol and 10% solutions of the substances in heptane. The values of the radius of the rotor calculated from Debye's theory are 1.41, 1.42, 1.40 and 1.43Å respectively. The rotor has been identified with the OH group.

The attenuation coefficients for the solutions in heptane were found to be greater than those of the pure liquids. This has been explained on the assumption that in pure liquids there exist dimers formed through intermolecular OH...O bond which break up in the solutions.

The absence of any absorption in the solutions of CCl_4 has been attributed to the formation of OH...Cl bond between the solvent and the solute molecules

INTRODUCTION

The study of the absorption of microwaves of wavelength 3.18 cms in *o*-chlorophenol (Ghosh, 1955) and in solutions in CCl_4 (Bhattacharyya, 1958) and similar investigations in ethylene chlorhydrin (Bhattacharyya, 1959) furnished evidence for the formation of hydrogen bond between neighbouring molecules in the pure liquids and breaking up of such associated groups into single molecule in solutions in suitable solvents. In the case of solution of ethylene chlorhydrin in methyl cyclohexane it was found that of the two types of dimers present in the liquid only those formed through the intermolecular OH...O bond break up into single molecules in the solution. There was no further interaction between solvent and the solute molecules, but in the case of the solution in CCl_4 it was found that an intermolecular OH...Cl bond is formed between the solvent and the solute molecules so that the C—Cl group at the other end of the latter molecule possesses freedom of rotation about the C—Cl bond These results confirmed the conclusions drawn by Mazumder (1959) from the results of investigations of the infrared spectra of the solution of ehylene chlorhydrin in CCl_4.

It was thought worthwhile to extend the investigation to other substances containing OH group as a substituent. Cyclopentanol and cyclohexanol which are two typical alicyclic alcohols were chosen for this purpose and the absorption of 3.18 cm microwaves in solutions of these two compounds in heptane and carbon tetrachloride has been investigated.

EXPERIMENTAL

The experimental arrangements and procedure were similar to those used in a previous investigation (Bhattacharyya, 1958)

In order to verify whether the absorption observed with any particular cell was genuine or spurious, two cells of different thicknesses were used successively and the strengths of absorption in the two cells were compared The absorption was studied in the pure liquids and also in 10% solutions of the liquids in CCl_4 and in heptane. The values of the static dielectric constants, the refractive indices and the coefficients of viscosity for the pure liquids were obtained from the standard tables. As the data for solution in heptane were not available they were determined experimentally In the case of the solutions in CCl_4 no absorption of the microwaves was observed

The radius of the rotor a, was calculated in the case of the pure liquids with the help of the Debye's formulae

$$\omega\tau = \frac{\epsilon_0+2}{\epsilon_1+2}\sqrt{\frac{\epsilon_1}{\epsilon_0}} \quad a^3 = \frac{KT}{4\pi\eta} \quad \ldots \quad (1)$$

where ϵ_0, the dielectric constant at very high frequencies has been taken to be the square of the refractive index of the liquid, ϵ_1 and η are the dielectric constant and the coefficient of viscosity of the liquid at the temperature $T°K$ at which the maximum absorption of the 3.18-cm waves takes place.

In the case of the solution in heptane also the same formulae and the constants determined experimentally were used.

RESULTS AND DISCUSSION

The temperature-dependence of the attenuation coefficient for the pure liquids has been shown in Fig. 1. Curves I and II are for two different cells filled with pure cyclopentanol. Similarly, curves III and IV show the absorption in pure cyclohexanol in the two cells.

Fig. 2. shows the relation between temperature and the attenuation coefficient for the 10% solutions of the cyclopentanol and cyclohexanol in heptane. In calculating attenuation coefficient for the solutions, the equivalent thickness of the substance in the cell instead of the real thickness of the cell has been taken into consideration.

The radius of the rotor calculated for the different samples are given in Table I. It is found to be about 1.4×10^{-8} cm in each case. The temperatures at which the maximum absorption take place in cyclopentanol and cyclohexanol are 96°C and 105°C respectively. From Fig 1 it is observed that the two cells of different thickness give identical results which show that the absorption is genuine.

TABLE I

Substances	$\omega/2\pi$ Mc/sec.	ε_1	$\sqrt{\varepsilon_0}$	$\tau \times 10^{11}$/sec	100η	T°K	$a \times 10^8$ cm
Cyclo-pentanol	9415	9.00	1.45	1.31	1.90	369	1.42
Cyclo-hexanol	,,	8.00	1.46	1.35	2.06	379	1.41
10% soln. of cyclo-pentanol in heptane	,,	6.00	1.43	1.48	1.70	281	1.40
10% soln. of cyclohexanol in heptane	,,	5.00	1.44	1.51	1.65	287	1.43

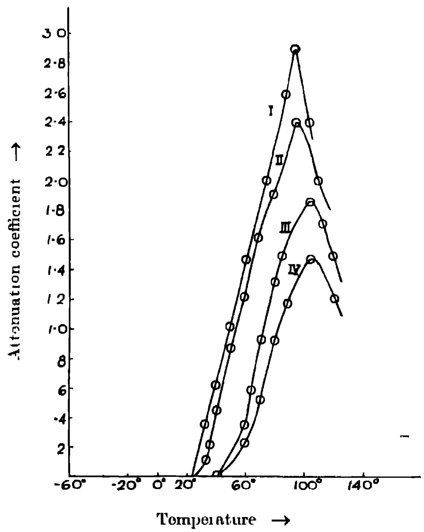

Fig. 1. Curve I—Pure cyclopentanol, thickness of the liquid = 1.4 cm.
Curve II— ,, ,, ,, ,, = 1.0 cm.
Curve III—Pure cyclohexanol, thickness of the liquid = 1.4 cm.
Curve IV— ,, ,, ,, ,, = 1.0 cm.

The fact that the solutions in heptane show the maximum absorption of the microwaves at much lower temperatures also lends additional support to the conclusions that the absorption is genuine and that it is dependent on the viscosity of the liquid, as postulated in Debye's theory. These results further show that Debye's formula is applicable in these cases

From Fig 2 it is observed that the values of the maximum attenuation coefficient for the solutions of cyclohexanol and cyclopentanol in heptane are 8 9 and 12 0 respectively. Fig 1 on the other hand shows the maximum values in the case of pure cyclohexanol and cyclopentanol to be 1 84 and 2 88 respectively The increase of absorption in the case of the solutions indicates the increase of the free OH group in solutions Hence it can be concluded that the OH group in large number of molecules in the pure substances have no freedom of orientation This can only happen if associated pairs of molecules are formed through intermolecular OH...O bonding. It can therefore be concluded that in the pure alcohols loose dimers are formed through intermolecular OH . O bond and they break up into single molecules in solutions

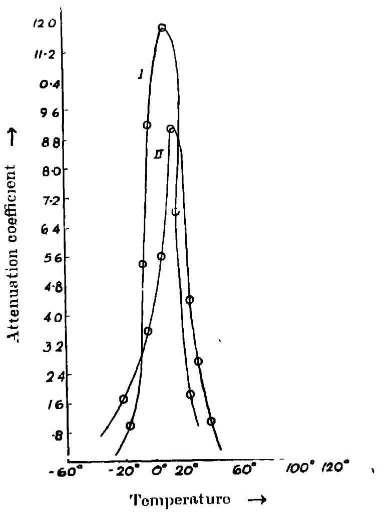

Fig. 2. Curve I—10% solution of cyclopentanol in heptane, (thickness of the cell = 1 4 cm.)
Curve II—10% solution of cyclohexanol in heptane, (thickness of the cell = 1 4 cm.)

In solutions in carbon tetrachloride, however, no absorption was observed though the viscosity of the solution in CCl_4 is nearly the same as that of the solution in heptane. It might be expected that the OH...O bond should break up in these solutions. Hence the absence of absorption indicates the formation of a new type of hydrogen bond due to the action of the solvent molecules It is quite probable that the OH group of the molecule of either of the compounds forms virtual linkage with the chlorine atom of the CCl_4 molecule in the solutions. This newly formed OH.. Cl bond prevents the free orientation of the OH group and consequently, no absorption of the microwaves can take place in these solutions. Evidence for the formation of such OH...Cl bond between the solvent and solute molecules in the solution of ethylene chlorhydrin in CCl_4 was observed earlier (Bhattacharyya, 1959). Study of the infrared absorption of the solution of ethylene chlorhydrin in CCl_4 (Mazumder, 1959) also led to these conclusions

The results of these investigations thus throw much light on the nature of influence of intermolecular fields in such polar liquids and their solutions in suitable solvents.

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